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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-lived halocarbon trends and budgets from atmospheric chemistry modelling constrained with measurements in polar firn" *by* P. Martinerie et al.

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Reply to Anonymous Referees

We are grateful to both referees for their comments, which helped improving the manuscript. Below we first discuss two points raised by both referees, then reply to other comments. Best efforts were made to take into account these comments without increasing too much the length of manuscript sections dealing with firn modelling.

Discussion of issues raised by both Referees

Preindustrial levels of CCl_4 and SF_6

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CCl_4 has the earliest anthropogenic emissions (starting in 1908) among our target gases and shows a peculiar behaviour in the firn: its concentrations are still important and show no decrease of the concentration - depth slope near the firn-ice transition. On the other hand, our chemistry model + firn model results, taking into account only anthropogenic emissions for building the atmospheric time trend scenario are generally consistent with the firn air data. This suggests that non-zero CCl_4 concentrations before 1908 are not required to explain the CCl_4 measurements in the firn. However, the high uncertainties on the CCl_4 lifetime and budget (Sect. 6.3 and Sect. 6.4) preclude a quantification of CCl_4 natural versus anthropogenic sources using our firn air data and models. Performing CCl_4 measurements in ice cores is likely the most direct way of fully answering this question.

SF_6 undergoes much smaller concentrations near the firn-ice transition: about 0.03-0.05 ppt at our Arctic sites, and 0.09-0.18 ppt at our Antarctic sites. A small natural SF_6 source from crustal degassing has been identified (e.g. Deeds et al., 2008, and references therein). Deeds et al. (2008) estimate the total lithospheric flux of SF_6 to be 13-80 kg/yr, which would sustain an atmospheric equilibrium concentration of 0.0004-0.0098 ppt with an SF_6 lifetime of 800-3200 years. To our knowledge, the lowest SF_6 concentration measured in firn air is 0.0063 ppt at Law Dome (Vollmer and Weiss, 2002). Our North GRIP record indicates a stabilization of SF_6 concentrations in the 74-78m depth range, however the suspicion of some contamination at 78m depth (Sect.5) and our detection limits (Sect.4) preclude a firm estimate of the pre-industrial SF_6 concentration from this site. Our North-GRIP data suggest that future high-precision SF_6 measurements in central Greenland firn air could help confirming the Law Dome result.

Our manuscript has been modified at p.994 l.4-5, p.1013 l.13-16, p.1014 l.13, and p.1021 l.25-28 in order to discuss more precisely the CCl_4 and SF_6 background levels.

N_2O atmospheric trend scenario used in Section 3.2

Both referees suggest that a more precise atmospheric trend scenario could be used in Section 3.2. N_2O is only used in this study in order to evaluate the vertical

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structure of the chemistry model atmosphere. A significant bias in model vertical transport would likely affect the sink magnitude of trace gases destroyed in the middle atmosphere. N_2O is used as a proxy of altitude in the Engel et al. (1998) compilation of balloon measurements for CFC-12. As these measurements were performed in 1978-1997, during which N_2O atmospheric trend records are available, our results should be only marginally affected by the ice-core part of the N_2O trend scenario. Following the two referees comments, a trend scenario for N_2O was built using MacFarling Meure et al. (2006) data. Although the Machida et al. (1995) record is more dispersed, the two smoothed scenarios are consistent within 0.5 ppb N_2O and result in differences in CFC-12 concentrations too small to be visible on Fig. 4 of our manuscript (less than 1ppt). A comparison with Fig. 3 in Battle et al. (1996) indicates that the atmospheric trend inferred from the South Pole firn record is about 2-3 ppb lower than our scenarios. Section 3.2 was modified to include these results (p. 1002 line 22 and p. 1003 line 4).

Reply to Anonymous Referee #1

p. 994, lines 4-5 (non-anthropogenic emissions) - corrected as suggested.

p. 994, line 18 and elsewhere - The world “recent” referred to our last firn drilling date (January 2003) which is confusing for SF_6. This has been modified p. 994, line 18, p 998 line 18, p1013 line 20, p1013 line 28, p1014 lines 2-3, p1021 lines 21-22 and on p7 of the Supplement (last paragraph).

p. 995, lines 3-4 (CMDL becoming ESRL) - Modified in the introduction and elsewhere, including the Supplement. The introduction now also mentions the previous acronyms of the trend measurement networks (CMDL, GAGE and ALE).

p. 996, line 11 (allows the discussion of) - Corrected

p. 1010, line 21 (Minor CFCs) - “Minor” changed to “Other”, Figure 10 captions also

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modified.

p. 1013, line 16 (CCl_4 "not inconsistent with") - The last 2 sentences of this paragraph were rephrased as follows: "Our atmospheric scenarios start with zero concentrations in 1907 and also lead to non zero modelled concentrations at the last measurement depths in the firn for all sites. Taking into account the uncertainties on the deep firn data and modelling discussed in Sect. 5, the overall consistency between the model and measured concentrations indicates that an atmospheric scenario with null CCl_4 concentrations before 1908 can account for the measurements in firn." (see also the above comment on CCl_4 and SF_6).

p. 1013 line 20. ("recent") - corrected as mentioned above.

p. 1016 lines 16-22 (CCl_4 ocean/soil sinks) - We agree with Referee #1 on the fact that an additional CCl_4 source may balance the ocean/soil sinks. From a non-speculative point of view, "Overall the budget of carbon tetrachloride remains poorly understood" (WMO, 2007). Our manuscript has been modified to emphasize this budget uncertainty. In future years (especially if the CFC-12 declining trend stabilizes), the comparison of trends in CFC-11, CFC-12 and CCl_4 might help to better constrain the "missing" CCl_4 source, as the "known" CCl_4 source is related to the declining CFC-11 and CFC-12 productions.

p. 1020 line 19 ("allows to translate") - corrected.

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p. 1002 line 15 (comparison with vertical atmospheric measurements) - a chemistry model bias on the transport of long-lived halocarbons to the middle atmosphere would affect their concentrations in their destruction zone, and thus the magnitude of their sink. This motivated the work presented in Section 3.2. The introduction of this section was completed to better emphasize this motivation.

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Estimate of the uncertainty ranges from the combination of several firn sites.
This cannot be done simply as our atmospheric concentration trends are not derived from the firn profiles but from emission scenarios and an atmospheric chemistry model ("bottom-up" approach). As our atmospheric concentration histories built independently from the measurements in firn, an envelope on the trends due to uncertainties on the firn data cannot be simply derived. On the other hand, efforts were made in this study to evaluate and discuss the uncertainties involved in our approach (e.g. Tables 3 and 5). A multi-sites inverse firn modelling ("top-down" approach) is possible but goes beyond the scope of this manuscript, which already uses a complex modelling approach (e.g. Fig. 1), as mentioned by Referee #2. Future work using a multi sites "top-down" approach would likely improve our knowledge on past halocarbon trends, and this is now mentioned in the conclusions section (p.1021 l.23). Including all available data in the minimization procedure (Law Dome, our FIRETRACC/CRYOSTAT sites, South Pole, ...) would provide the best constraint. As some uncertainties due to the firn model setup (e.g. diffusivity, impact of model setup on age structure, etc.) are not taken into account in the envelopes derived from inverse firn models, using and comparing different firn models might also be useful.

Effect of different atmospheric trend scenarios on CFC-114 in firn (with a special focus on the Dome C lock-in zone).
While having a close look at the comparison with Sturrock et al. (2002) scenarios at Dome C (Fig. 10), an inconsistency in the slope evolution of the firn model results around 95m depth was noticed between results obtained with our scenarios and Sturrock et al. (2002) scenarios. An error was found in the diffusivity profile used for the Dome C simulations with Sturrock et al. (2002) scenarios. Figures 10 and 11 have been redrawn using the correct (best fit) diffusivity profile at Dome C for all scenarios. Although not directly affecting our conclusions, this emphasizes the effect of uncertainties on firn modelling (see also the comment on diffusion coefficients below). In the case of CFC-114, the difference between the Sturrock et al. (2002) firn data based scenario and our emission-based scenario is complex, because its sign changes around

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1985. Looking first at species for which the differences between scenarios is mostly concentrated in 1970-1985 and does not change sign: CFC-113 and CFC-115, the low accumulation rate sites (Dronning Maud Land and Dome C) show a higher sensitivity to the differences in scenarios than sites with higher accumulation rates (Fig. 10). However, this sensitivity decreases near the firn-ice transition. CFC-114, for which the scenarios show highest differences around 1950-1970 is the trace gas species most affected by the scenario used at the deepest sampling levels. In this case, Greenland sites (with higher accumulation rates) are more affected than Antarctic sites. This suggests that the sensitivity of different firn sites to the concentration trend history may be time-dependent. Although their low age spread likely renders the very high accumulation rate Law Dome sites especially suitable for trend scenario estimate, additional precision might thus be gained from the joint use of other sites. Overall, the Sturrock et al. (2002) scenarios derived from firn data are mostly consistent with our emission based scenarios, especially when considering the budget uncertainties on CFC-114 and CFC-115 (Table 5). Due to these uncertainties, we are reluctant to add a more detailed discussion of CFC-114 scenarios (especially in the lock-in zone were uncertainties are at their maximum). Changes were made in Section 6.2.2 to emphasize less the differences between scenarios and more their general consistency (p.1011 l.20, 26, 29, and p.1012 l.5-6).

p. 995 line 15 (wording confusing) - modified.

p. 995 line 7-12 (clarify the processes at work in firn) - slightly modified in the aim of keeping the general introduction brief and easily understandable for non firn specialists.

p. 999 (Section 2.2, clarify the processes at work in firn, lock-in zone underemphasized) - first paragraph modified.

p. 1000 line 29 (How accurate are the molecular diffusion coefficients?) - Up to now, halocarbon diffusion coefficients in air have been calculated by the firn modelling com-

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munity using theoretical formulas generally based on estimates of molecular volumes. The accuracy of these calculations can be estimated by comparison with available measurements for other chemical species (e.g. Fuller et al., 1966). The question of Referee #2 led us to have a closer look at the bibliography and find a consistent set of diffusion coefficients measurements for CFCs, SF_6, CO_2 and CH_4 (Matsunaga et al., 1993, 1998, 2002). Our calculated diffusion coefficients are now evaluated against these data in the supplementary material. For a more consistent comparison with Sturrock et al. (2002) atmospheric trend scenarios, derived from inverse firn modelling using calculated diffusion coefficients, we still use our initial diffusion coefficients in the manuscript. The differences with firn model results obtained using measured diffusion coefficients mostly affect deep firn layers, and remain within the uncertainty range due to firn data dispersion, firn diffusivity and atmospheric trend estimates. We now mention that the effect of the uncertainty on CFC-113 diffusion coefficient is of similar magnitude as the effect of differences in atmospheric trend scenarios for CFC-113 (p.1011 l.20).

p. 1005 line 1. (which results - the simulated vertical profiles?) - yes, corrected.

p. 1005 line 6. (which trace gases were used to constrain the firn diffusivity profiles?) - The diffusivities are calculated using inverse firn modelling constrained with CH_4 at all sites except Dome C, where CO_2 is used because the diffusivity calculated with CH_4 produces a too steep slope break around 95m depth, as described in the supplementary material. The gas used for diffusivity calculation now clearly appears in Section 2.2 (p. 1000 line 17). "typically CO_2 or CH_4" in the introduction has been replaced with "such as CO_2 or CH_4". The atmospheric trend scenarios used to constrain the diffusivity calculation are described in Fabre et al. (2000) as mentioned in the legend of supplementary Fig. 2. A comparison of these scenarios with scenarios calculated from MacFarling Meure et al. (2006) data was performed and is now described in the supplement. The results are consistent within the uncertainties on the MacFarling Meure et al. (2006) ice core data. This Referee's comment mentions the flattening of the CO_2

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trend around 1940-1950 as a possible reason for the better results obtained with diffusivities calculated with CH_4. We should note that a reduction in the slope of the CH_4 trend is also suggested by the MacFarling Meure et al. (2006) data for this period. A quick test was performed using a stronger smoothing of the CO_2 trend scenario, and this did not affect our results. It is likely due to the fact that the age distributions in firn are wider than 10 years for that period at our drilling sites. CFC-11 and CFC-12 are not used to constrain the firn diffusivity profiles. However, as the uncertainties on their emission histories, and thus their calculated historical trends are likely to be relatively small, they are used to discuss the firn model evaluation. The above modifications and a change at p. 1005 line 7 should make this point clearer in the manuscript.

p. 1005 l.8 (for firn model validation?) - yes, modified.

p. 1005 l.9 (experimental data meaning measured concentrations?) - yes, modified.

p. 1005 l.22 (Were melt layers actually observed at this depth?) - yes, but as between all firn air pumping depths: 197 melt layers with thicknesses ranging between 0.5 and 6.5 cm were logged in the Devon Island firn core. The thickest melt layer was found at 28m depth, i.e. in the 25-30m depth range where a drop in the concentrations of major CFCs is observed. On the other hand, the highest concentration of melt layers between two firn air pumping levels (29 layers with 50 cm cumulated width) is observed between 16 and 20m depth. Although two 5 cm thick and two 4cm thick melt layers were observed between these depths, halocarbon concentrations show no drop. However, the 13m-30m region, which includes the two above depth intervals, is the only place in the core showing more than 20 melt layers with cumulated widths exceeding 25 cm per firn air pumping interval. The effect of melt layers is probably affected not only by their frequency of occurrence and width but also by their horizontal extent and continuity which cannot be assessed from the firn core stratigraphy. The manuscript was modified in order to better describe melt layers in the Devon Island firn core.

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p. 1005 l.25 and elsewhere (replace experimental with measured or observed) - corrected.

p. 1006 l.2 (the atmospheric concentration scenario?) - yes, modified.

p. 1006 l.6-7 (gentle slopes / steeper slopes) - corrected.

p. 1006 l.27 (the particular trace gas) - modified.

p. 1007 l.7 (the firn ages do not always increase with decreasing diffusivity) - Modified. The increasing ages with decreasing trace gas diffusion coefficient only applies to the model-derived “firn age”. The “scenario age” calculated from the observed concentration in firn and atmospheric time trend is affected by data dispersion of the concentration measurements, especially in the deep firn.

p. 1007 l.11 (why should the gases of interest have similar mean and scenario ages?) - Modified - The “scenario age” (or effective age) should be identical to the mean age only for a trace gas undergoing a linear growth rate in the atmosphere (Trudinger et al., 2002). The difference between these two ages increases with the width of the age distribution and the non-linearity of the atmospheric trends.

p. 1008 l.3 (globally /generally) - corrected.

p. 1008 l.15 (what does “the regularity of the depth-age profile” mean?) - Modified. The Devon Island mean age-depth profile (Fig. 6) does not show contrasted gentle/steep slope regions. Moreover, it has the lowest age-depth gradients in the deep firn.

p. 1008 l.16 (Would not impermeable melt layers reduce the age spread?) - This is likely the direct effect of melt layers, however, as mentioned above, it is limited by their horizontal extent and continuity which cannot be easily assessed. We should note that heterogeneities in firn are not directly taken into account in our model (as discussed in Sect. 2.2). On the other hand Devon Island has the lowest diffusivities among the five sites, which may lead to increased age mixing at equivalent depths. There is no direct way to evaluate the reliability of modelled age spreads. The consistency of model

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results with observations for trace gases with different atmospheric trend histories and different diffusion speeds indirectly suggests that the modelled age structure at Devon Island is realistic.

p. 1008 l.22 (time of drilling) - modified.

p. 1008 l.26 (of widening for sites with lower snow accumulation) - modified.

p. 1010 l.25 (delete trend) - corrected.

p. 1010 l.26 (there are not) - corrected.

p. 1010 l.26 (which is the studied period?) - before 2003 (i.e. our last drill date), modified.

p. 1010 l.27 (which recent data - for what years?) - the Cape Grim air archive (as illustrated in the Supplement), corrected.

p. 1011 l.28 (model-data differences) - corrected.

p. 1012 l.2 (slope break/change) - corrected.

p. 1012 l.15-18 (could not follow the reasoning behind the lowest CFC-113 concentration argument) - Halocarbon concentrations measured near the firn-ice transition at Law Dome (DSSW20K) are lower than ours (even at Arctic sites) for all species except CFC-113, for which similar concentrations are obtained in the two studies. Modified.

p. 1014 l.2 of Sect. 6.3 (abundance is calculated from concentration ...). Modified.

p. 1014 l.3 of Sect. 6.3 (loss rate and proportional) - corrected.

p. 1014 l.28 and elsewhere (region instead of area or place) - modified.

p. 1015 l.5 (a homogeneous) - corrected.

p. 1015 l.18 (what is meant by “normally”?) - “normally” suppressed.

p. 1016 l.23 (delete “time”) - corrected.

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p. 1017 l.17 (+140) - modified.

p. 1017 l.26 (equivalent to) - modified.

p. 1018 l.7 (globally/generally) - modified.

p. 1019 l.25 (are also shown) - corrected.

p. 1020 l.6 (compare to total radiative forcing for long lived greenhouse gases) - modified.

p. 1021 l.23 (emission or concentration?) - concentration, modified.

p. 1022 l.15 (budget histories) - modified.

p. 1022 l.21 (insufficiently) - corrected.

Is the last sentence in the conclusions rather obvious for any atmospheric compound? - this is true for species with positive atmospheric concentration trends at the time scale of their atmospheric residence times. This sentence has been completed.

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